fibrous (high aspect ratio) forms. This morphological progression can be continuous from equant particles to the asbestos form.

All these forms have essentially the same chemistry and crystal structure. If any of these elongated particles is made airborne and assessed by any of the current regulatory or ISO methods for phase contrast microscopy (PCM), scanning electron microscopy (SEM) or transmission electron m microscopy (TEM) analysis of asbestos fibres it would be counted and classified as an asbestos fibres.

This problem of including cleavage fragments and other growth forms in the assessment of the asbestos risk, had been recognised for many years but due to the measurement methods being applied were primarily to assess the level of control and risk in the asbestos manufacturing and user industries, this potential interference was not considered important.

3.3 OSHA Rulemaking

The US Dept. of Labour occupational safety and health administration (OSHA) first regulated asbestos in 1971 (OSHA, 1971) by adopting an emergency temporary standard. When a formal rulemaking on asbestos in 1972 included non-asbestiform fibres of anthophyllite, tremolite and actinolite, the distinction between asbestos and non-asbestos fibre became important; especially for some mineral products (e.g. Lake Superior taconite and New York talc) which contained amphibole particles which may have been cleavage fragments or fibres. This started a protracted series of legal challenges, petitions and stays for the next 20 years by the talc and mineral industries of the USA. OSHA subsequently made clarifying revisions to distinguish between 'non asbestiform talc' and 'fibrous talc' and tremolite. In 1974 OSHA agreed to interpret 'asbestiform tremolite' as being fibres with aspect ratios >5:1 (instead of 3:1) however preliminary data gathered by NIOSH (Dement and Zumwalde, 1976) at talc mines showed detrimental health effects leading to the cancellation of this distinction in 1977.

This situation emphasised the need to differentiate between cleavage fragments and asbestos and led to calls to increase the aspect ratio in the morphological definition of asbestos fibres (e.g. Campbell et al., 1979, Walton, 1982, McCrone, 1987, Wylie, 1990, Langer et al, 1991). The stone and mineral producers have enthusiastically supported such calls (both through their associations' submissions to regulatory agencies (OSHA, 1994) and through support to various researchers. The industrial mineral producers associations contended that elongated mineral cleavage fragments of amphiboles produced by their activities are not asbestos and these fragments represent no additional hazard other than that of a nuisance dust. Therefore their products should be excluded from any asbestos regulation or rule making.

After a sustained campaign non-asbestiform tremolite, anthophyllite and actinolite were removed from the OSHA rule in 1992 (OSHA 1992). In this rule making, OSHA

determined that, "evidence is lacking to conclude that non-asbestiform tremolite, anthophyllite and actinolite present the same type or magnitude of health effect as asbestos and failure to regulate them as asbestos does not present a significant risk to employees".

However, as no change in the regulatory definitions was made and no method given to characterise particles as asbestos fibres or elongated mineral fragments, the question of what is an asbestos and a non-asbestos cleavage fragment, remained unresolved for any practical assessment of hazard or risk. OSHA in its last rule making in 1994 emphasised the need to regulate asbestos in soils and also published a non-mandatory method (ID-191) which included a description of what OSHA considers as countable asbestos.

3.4 Measurement of risk from asbestos

There are 14 epidemiological studies of asbestos workers and miners, where some exposure measurements are available and have been compared with mortality data to give a dose -response relationship. The exposure measurements are generally very limited and are broad conversions from a variety of measurement methods. These data sets has been interpreted many times, with the review by Doll and Peto in 1985 forming the basis for the current UK control limits in the Control of Asbestos at Work Regulations (CAWR, amended 1992) designed to limit the risk from airborne asbestos exposures. The Doll and Peto analysis of the data found that crocidolite is a more potent carcinogen than chrysotile with amosite somewhere in between. Although no other asbestos type has epidemiological data, tremolite asbestos which is a minor contaminant of chrysotile has been argued to be a potent carcinogenic fibre for the chrysotile mining community (McDonald et al. 1997) and for some environmental exposures (Yazicioglu et al. 1980, Baris et al, 1988). It has also been described as one of the most potent carcinogenic fibres used in animal inhalation tests (Davies at al. 1980).

The current European reference method for airborne asbestos risk assessment, is set out in annexe 1 of EC directive 83/477/EEC and implemented by MDHS 39/4 uses X400 -X500 phase contrast microscopy (PCM) counts of visible >5 µm long fibres (particles with aspect ratio >3:1 and < 3 µm width) collected onto a membrane filter from a known volume of air. The method currently does not allow discrimination between fibre types and excludes fibres attached to >3 µm particles, as they are deemed as non-respirable. Future changes with the expected introduction of a new WHO (1997) method for assessing all fibres by a single set of counting rules, allow for the discrimination of fibre types when assessing risk and the inclusion of attached fibres in the count. This will make it easier to relate hazard and risk estimates but fibres with widths > 3 µm will continue to be included only in the hazard assessment. The number of > 3 µm wide fibres are often insignificant in terms of fibre count but will be very significant if include in the fibre mass estimate of hazard

3.5 Research questions for hazard and risk assessment

To resolve some of the above difficulties and to develop a method for assessing the hazard the following questions were addressed in the next section of the report.

1. What are the differences between amphibole fibres and asbestos?

2. How can these differences be exploited to produce a method which is capable of discriminating between asbestos and non-asbestos fibres?

3. Is a discrimination between amphibole fibres and asbestos fibres justified on health grounds? (i.e. what is the evidence that shows that a 0.5μm wide 20 um long acicular fibre has less fibrogenic and carcinogenic potential in the lung, than an amphibole asbestos fibre with exactly the same dimensions)

4. THE DIFFERENCES BETWEEN AMPHIBOLE ASBESTOS FIBRES AND OTHER FIBROUS FORMS OF ASBESTOS.

An in-depth review of the differences has already been carried out and reported in IR/L/MF/95/16. The review looked at such factors as: size distribution, aspect ratio distribution, morphology and habit, chemical differences, SAED patterns, particle orientations and structural defects. It concluded that although some of these are useful indicators, especially if they can be used in conjunction with each other they can only be used with anything approaching good reliability to characterise a population of particles.

Finding a means of categorising individual particles (regardless of cost) was found to be elusive. The review concluded that the examination of the frequency of (100) twin boundary faults in the crystal lattice had most to offer as a definitive test. The review also concluded that work carried out under this project report IR/L/MD/11/95 viewing the end morphology of the fibre could also provide an excellent guide but was limited in its application.

It was acknowledged that neither of these approaches would be simple and rapid enough for routine use. Measurements of size and aspect ratio carefully and critically applied may give a good indication of the asbestos fibre content in a population of elongated particles.

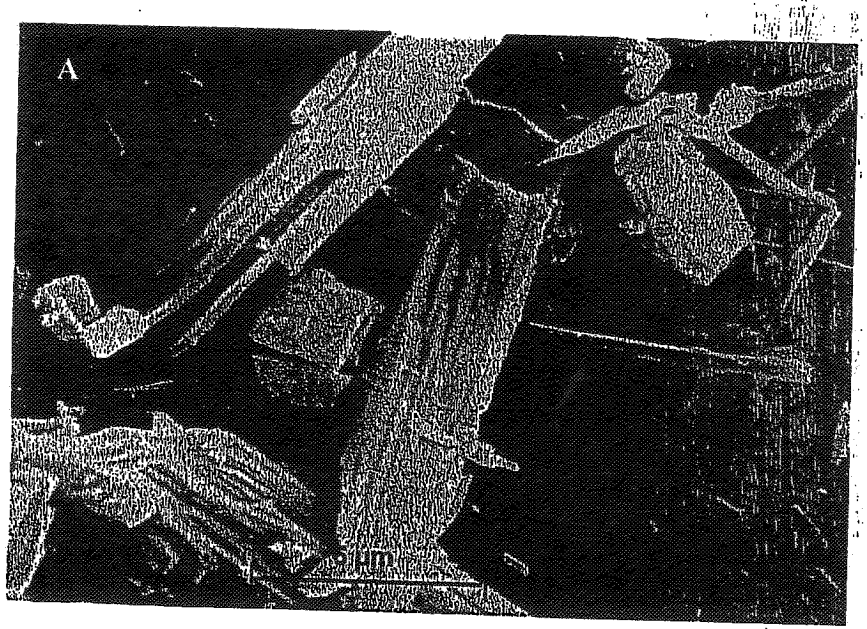
4.1 Methods for individual fibre-by-fibre characterisation

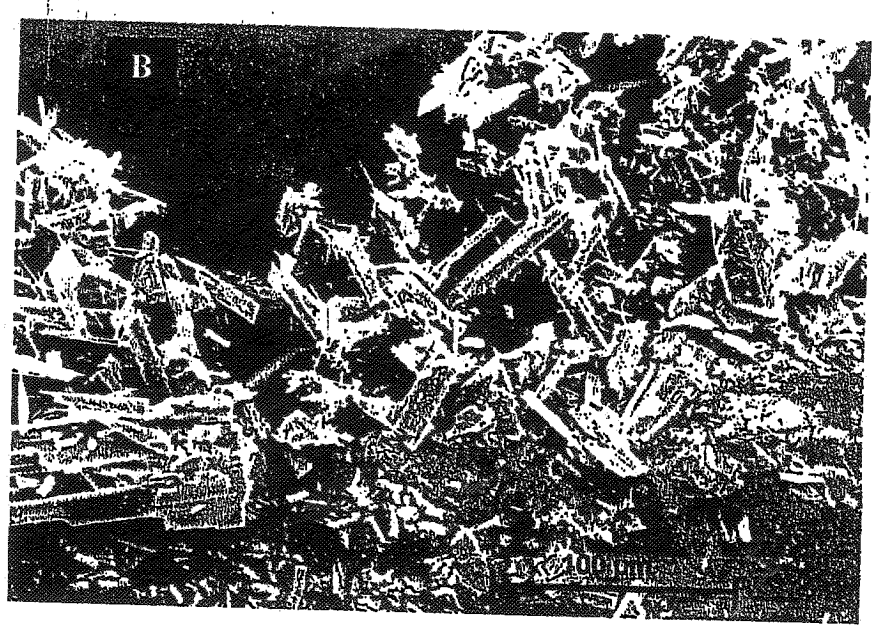
4.1.1 Fibre morphology

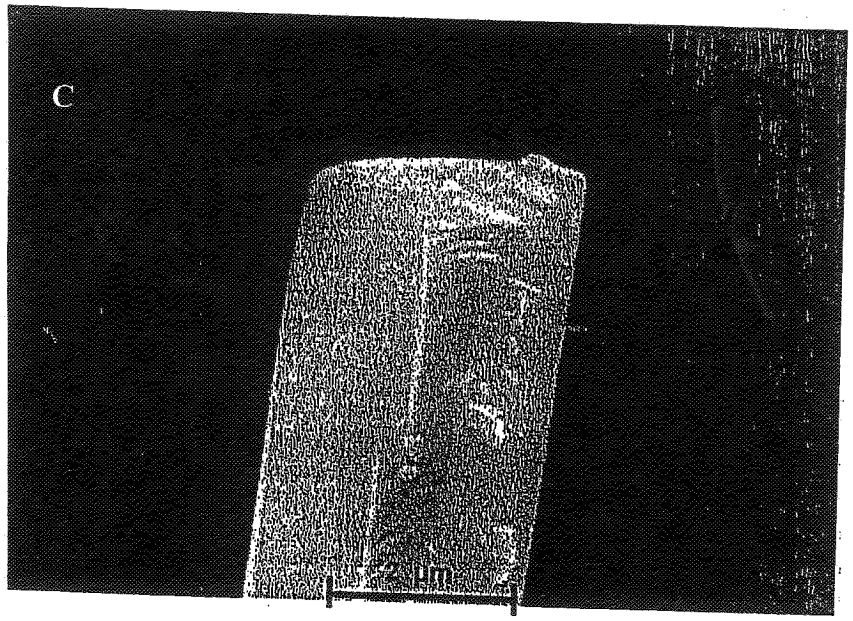
When fibres are collected or placed on a substrate and viewed in the microscope they usually rest on their long axis (the c-axis of the crystal) and are at right angles to the incident light or electrons. This is why aspect ratio is used as the primary feature for recognition. In optical microscopy, split or splayed ends of large fibres are usually taken as strong evidence that the fibres are asbestos. Therefore, when viewing fibres by optical microscopy with widths of several micrometers some evidence that it was a fibre bundle would be expected. Most fibre seen will often be much thinner and will not show this characteristic due to the limited resolution of the PCM/PLM, the fibre not being fibrilised or is incapable of further splitting.

Improved resolution and 3D morphology are obtained by SEM (Plates 1-5), but to view the fibril structure it is necessary to look down the c-axis (the end of the fibre). This can be achieved mounting selected bundles of fibres in near vertical position so it can be viewed straight down the c-axis, by adjusting the stage tilt. Alternatively, fibres aligned on a filter with a Prodi spectrometer can be mounted on a 45 degree stub so to give a high angle of tilt, so with further stage tilt can be viewed at an acute angle to the c-axis. Both methods rely on a high degree of fibre alignment and either method makes it possible to study some individual fibres morphologies, but cannot be routinely applied to all fibres..

Plate 1: Tremolite:- (Edenitic) Drumnadrochit; HSL82075/95.







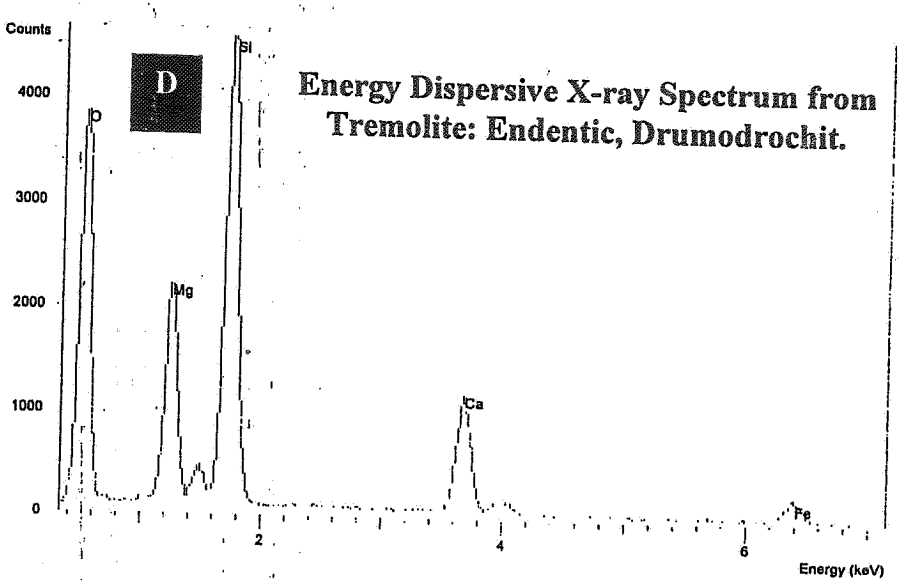
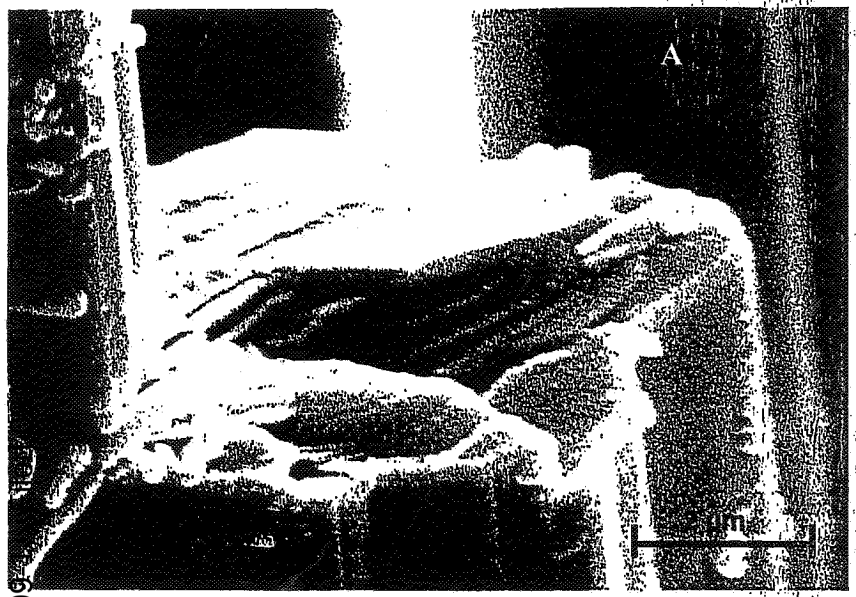
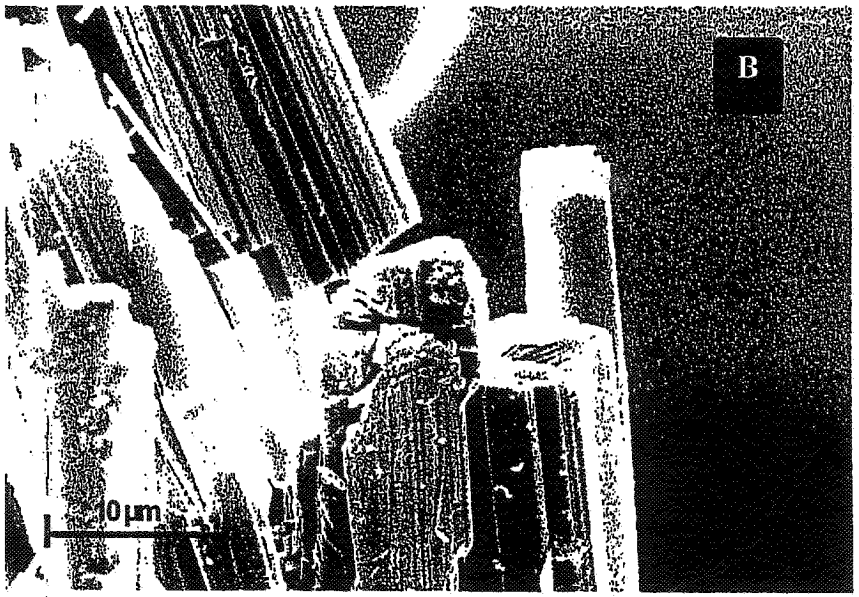
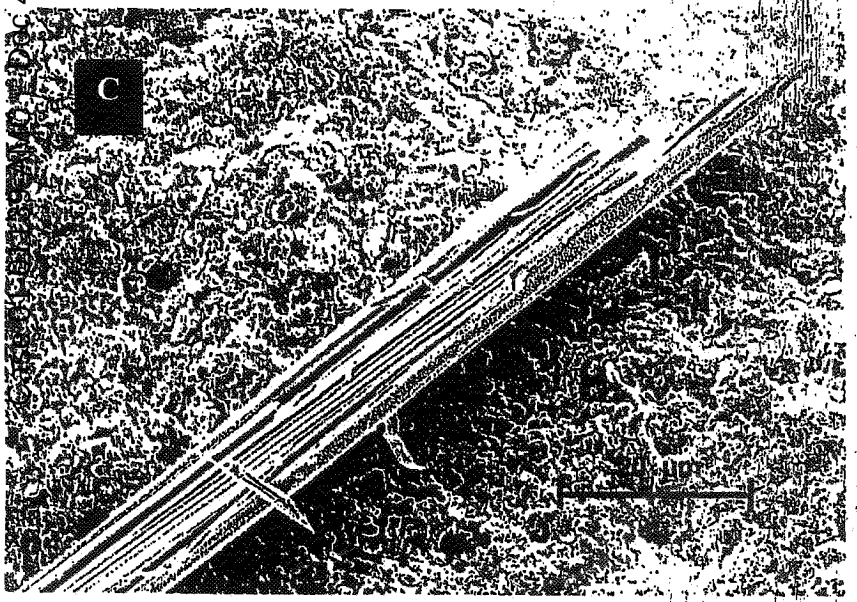
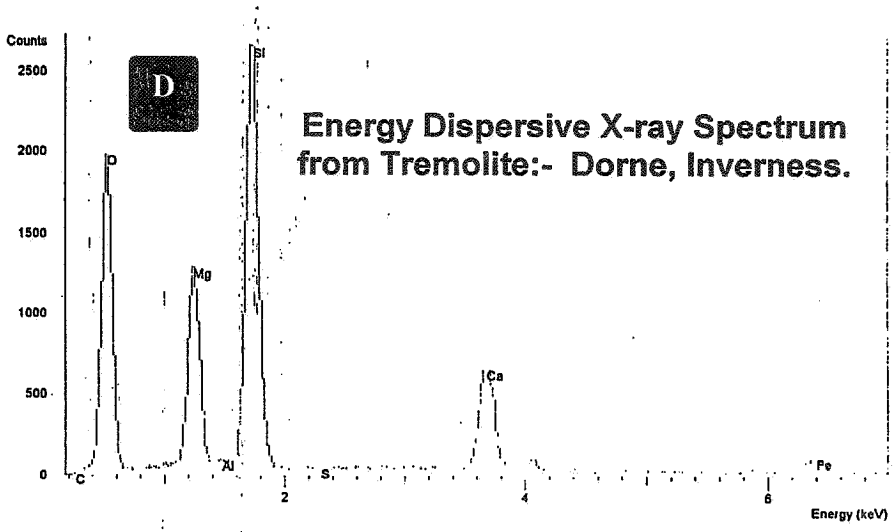


Plate 2:: Tremolite:- Dorne, Inverness; HSL82074/95.



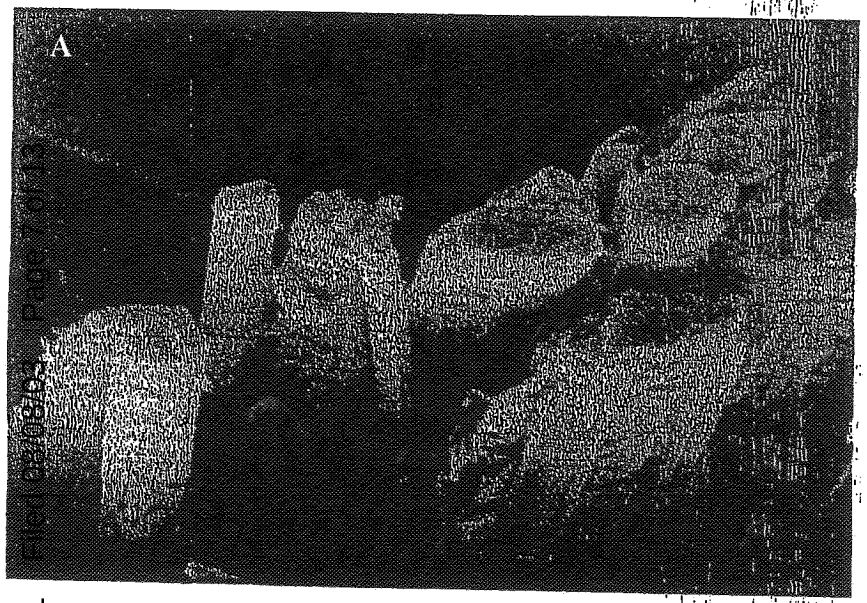


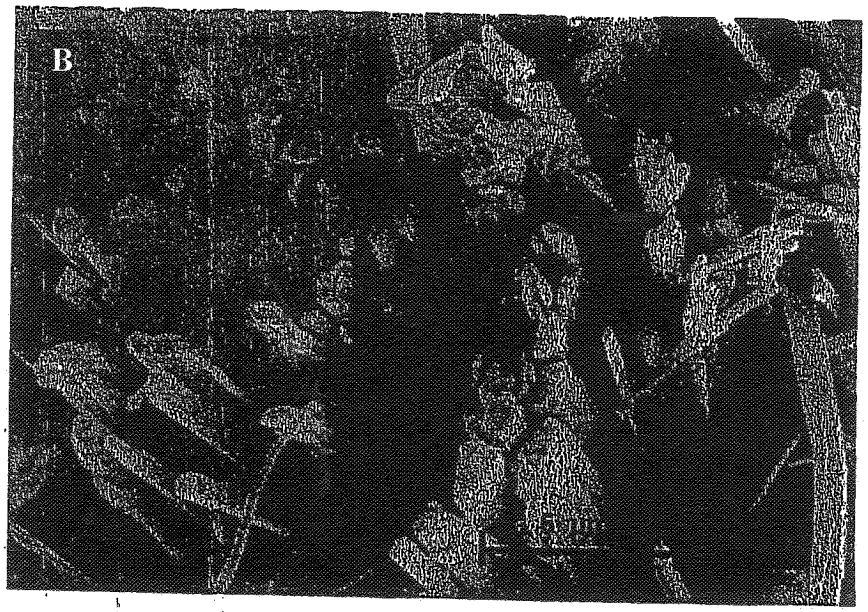


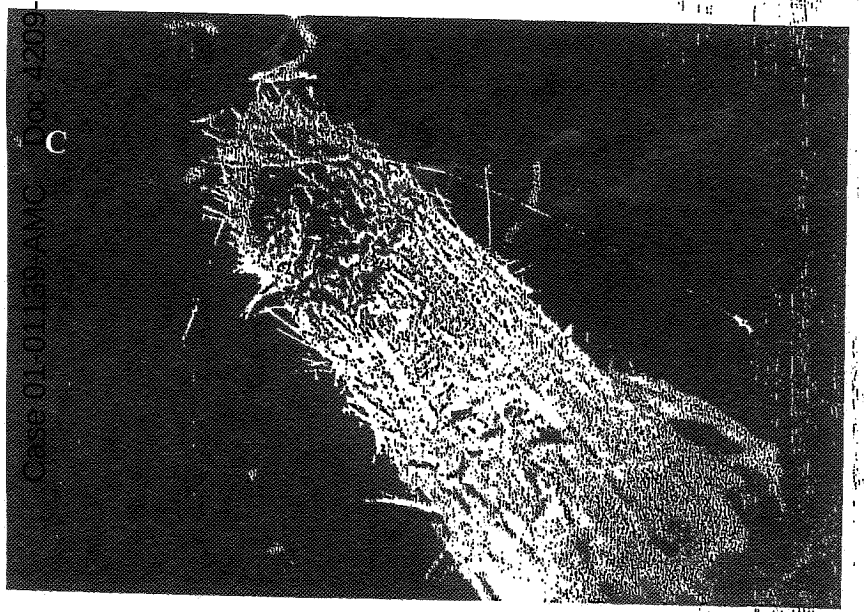


Energy Dispersive X-ray Spectrum from Tremolite:- Dorne, Inverness.

Plate 4: SEM end morphology of tremolite asbestos:- Rajahstan "White"; (HSL82072/95): .







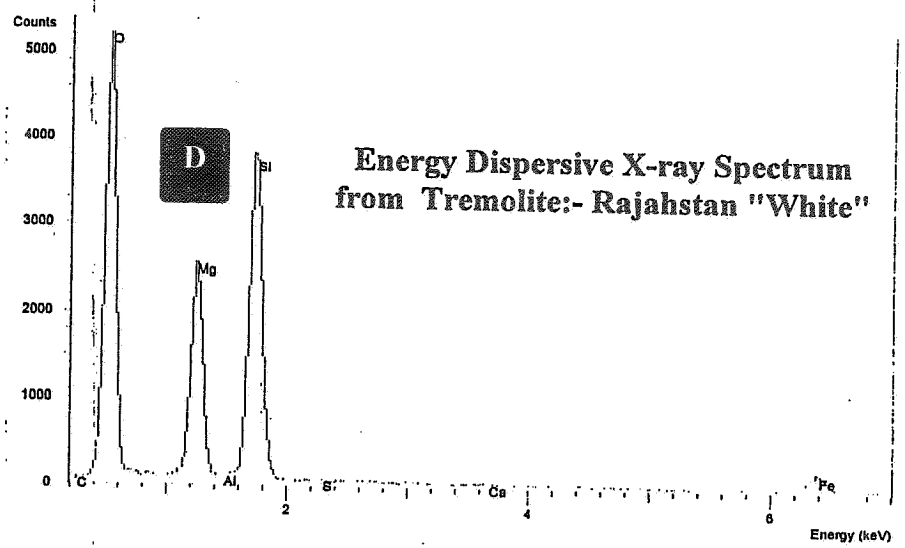
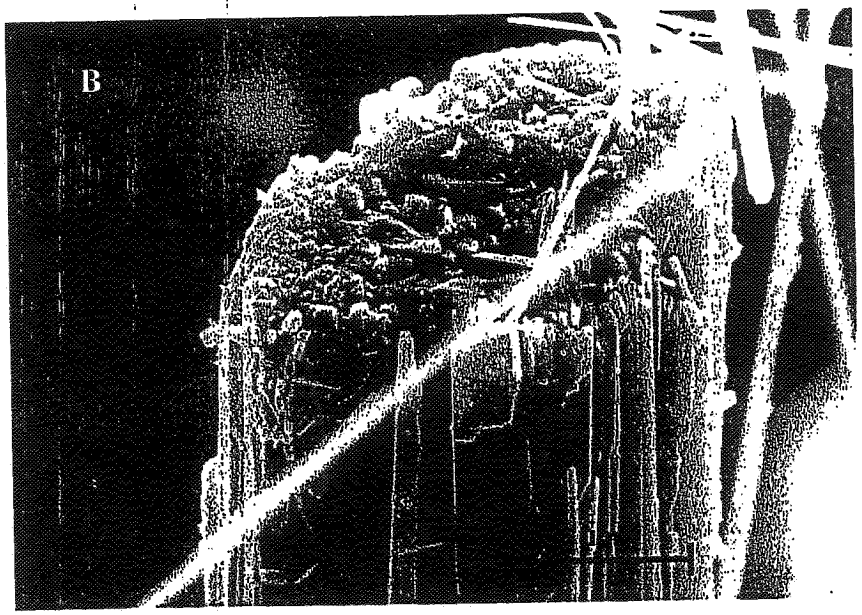
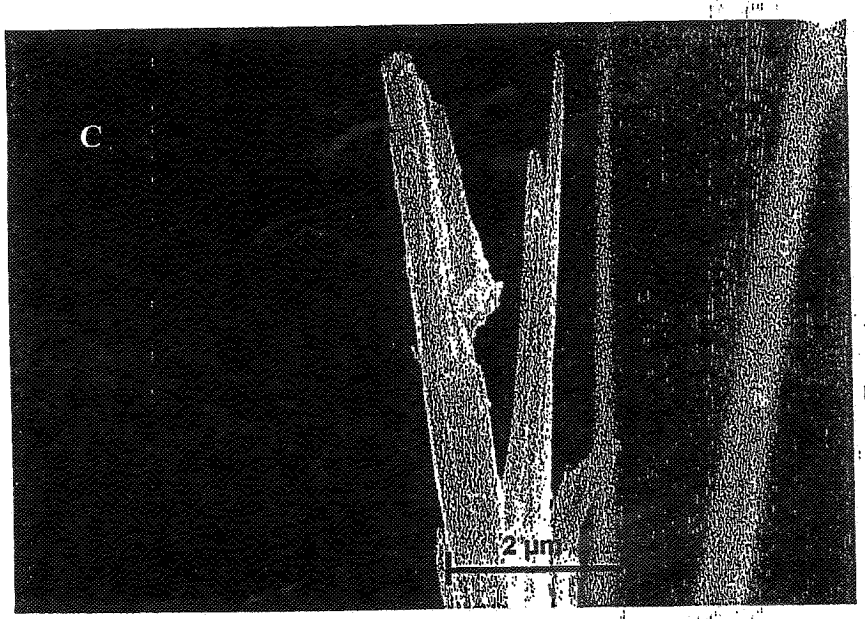
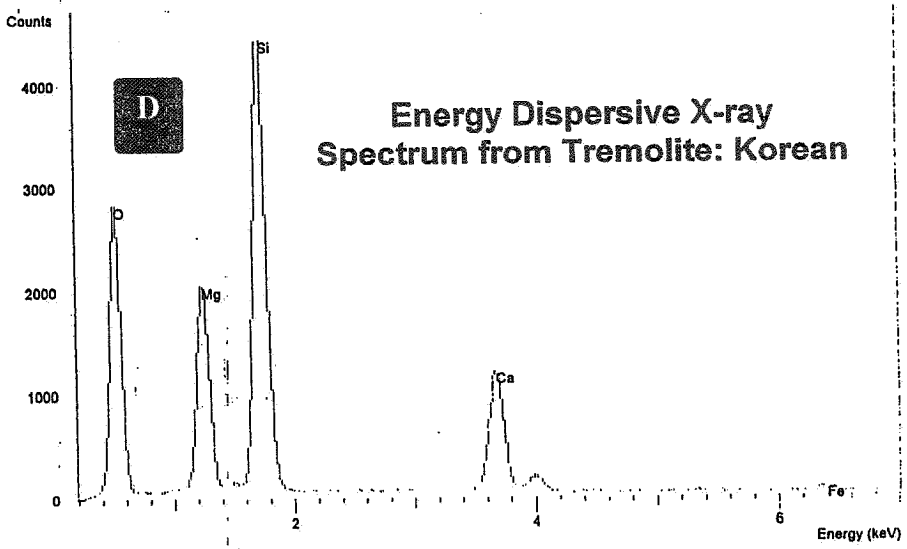


Plate 5: SEM end morphology of tremolite asbestos:- Korean (HSL82068/95)







4.1.2 PLM identification

Optical properties of fibres in polarised light are used to identify the mineral type (MDHS 77). This is done by picking out representative fibres during a low power, stereo microscope evaluation and mounting in a refractive index oil, close to that of the possible asbestos type and a series of observations made to determine the morphology, colour and pleochroism (if present), birefringence, extinction characteristics, sign of elongation and refractive index. A trained and experienced microscopist can reliably identify asbestos using the above properties although it may be difficult to distinguish between tremolite and actinolite asbestos.

Use of an optical microscope implies a lower limit to which the width can be reliably detected, measured and identified. For phase contrast microscopy evaluations the limit of detection at x500 is about 0.2 - 0.3μm (MDHS 39/4). Phase contrast optics also distort the image forming a halo which makes it difficult to size thin fibres and gives a bias towards overestimation of the width. The thickness of the fibre and its birefringence also limit the ability to identify the fibre, particularly in the case of crocidolite and actinolite. In general for polarised light microscopy identification of asbestos (MDHS 77) only fibres with widths >0.8 um can be identified. Quantitative phase contrast microscopy evaluations (MDHS 39/4) of airborne asbestos samples onto membrane filters, rarely count more than 5% of the chrysotile and crocidolite fibres present and only a small percentage of these are likely to have widths sufficiently large to allow the fibres to be discriminated (MDHS 87).

4.1.3 PLM extinction angle

A single biaxaial prismatic crystal will show an extinction angle of -15 to +15 ° depending on its orientation around the prism axis (c-axis). The maximum extinction angle, which is characteristic of the mineral since it defines or is defined by the orientation of the principal refractive r.i.'s relative to the crystallographic axes, is observed in only one orientation, that with (010) parallel to the microscope stage. The extinction angle is zero (straight extinction) only when (100) is parallel to the microscope stage. Intermediate values of the extinction angle are observed in intermediate orientations. An amphibole asbestos fibre consists of many single crystal fibres with their c-axes aligned but in random orientations around that axis. The individual fibres will have randomly varying extinction angles between -15° and +15° and their cumulative effect gives the fibre bundle zero extinction angle (straight extinction). Therefore as a first approximation fibres which give straight extinction are probably asbestos.

To be sure that straight extinction is not the result of a single crystal being in or near the orientation with (100) parallel to the stage, it is necessary to roll the fibre which is not routinely achievable or practicable. Further uncertainties arise because it is difficult to distinguish between a small extinction angle and straight extinction and an asbestos fibre with only a small number of single crystal fibres may not average out to

zero. Moreover, if there is twinning (as amphiboles frequently are) the extinction angle will be reduced to $<5^0$, making it difficult to be definitive. Therefore extinction angle does not provide a reliable fibre-by-fibre classification for asbestos fibres.

4.1.4 *High resolution TEM / Crystallographic techniques*

A high density of (100) twin lamellae is indicative of amphibole asbestos but is difficult to study as precise orientation of the fibre is required. This type of analysis conventionally takes tens of minutes per fibre but the advent of on- board measurement systems and computer controlled software with the ability to find zone axis orientations, does make this technically feasible to attempt. However, the technique is limited to thin samples as fibres >0.2μm thick could not be analysed. Thin fibres also represent only a small proportion of the asbestos mass and the method would not be useful for mass estimates. Also, the frequency of (100) twins as an important determinant of asbestos is also uncertain. It might hold true for amosite but the frequency of twins is much less for crocidolite and may be almost absent in tremolite asbestos (Whitaker, 1979). Tremolite is by far the most frequent contaminant fibre that that method would be required to adjudicate.

Langer et al., 1991 published TEM criteria to discriminate tremolite asbestos from cleavage fragments stressing the importance of the (100) and (010) twin planes, which appear to simple observation to produce a relative insensitivity of the electron diffraction net to tilting and the relative occurrence of different zone axes. They also recognise that TEM analysis was limited and there was no unique feature which can be used by microscopical investigations to determine whether a fibre is asbestos or not. One important use of the high resolution TEM described was to determine whether the crystal structure is that of an amphibole or a biopyriobole, which is the case in some New York talc deposits.

4.1.5 *Fibre chemistry*

Accurate chemistry of minerals is usually established by mineralogists using electron microprobes. SEM and TEM analysis relies on the use of energy dispersive x-ray analysis (EDXA) to determine the elemental composition (usually the element to silicon ratios) to identify individual fibres. This is less accurate and precise and depending on the type of detector may give no or limited information below atomic number 11. As outlined in section 2.2.2. the chemical definitions for the mineral types have changed somewhat and the new definitions based on a 50% line between compositions may give considerable scope for deciding that the chemical composition may not be exactly that of the regulated asbestos mineral type. Therefore, considerable stability of the chemistry of individual fibres and equipment is necessary if a laboratory seeks to rigorously apply the IMA chemical nomenclature. Such rigorous classification could be justified mineralogically and legally but

practically and scientifically these cannot be achieved. Also one must question whether the human body itself can recognise whether if 1% more Fe is substituted for Mg in an actinolite fibre, the fibre is no longer carcinogenic.

In practice, the precision of the EDXA analysis needs to be established e.g. Clark et al. 1995 using a TEM -EDXA system found variations in the Mg:Si ratios of chrysotile, amosite and crocidolite standards of between 60 - 78, 8 - 12 and 2 - 5 % for the 10th and 90th percentile respectively. Even if these limits were used, 1 out of every 5 asbestos fibres seen from their standard would be rejected. Therefore realistic limits for the chemistry need to be applied and must be based on a detailed calibration of the performance of the equipment in use, against known standards. Even then attached particles or other coatings may interfere with individual fibre analysis and a degree of judgement is required other than just the elemental ratios. The detector performance, on a day to day basis must also be rigorously monitored to ensure the standard parameters established are still valid. The SEM-EDXA which uses 'thick' samples and larger probes, will have poorer precision and be subject to much greater interference from the sample than the TEM-EDXA method.

Chemistry is an important determinant of whether the fibres are classified as asbestos or non-asbestos for regulatory purposes. Chemistry can be used to distinguish between fibres formed from different minerals if there is a significant difference between their chemistries. It cannot distinguish between whether a fibre is asbestos or non - asbestos if the fibre is formed from the same mineral, as is frequently the case for many mined and quarried products. What is accepted as a positive chemical identification of an asbestos fibre needs careful consideration on a site-by-site basis.

4.1.6 *Other fibre chemistry methods*

There may be other possibilities outside the scope of this project for using chemistry to distinguish between fibre type. For instance there may be some differences in the surface chemistries of asbestos fibres reflecting the special growth conditions, which they have undergone. Raman infra-red microscopy, and secondary ion mass spectroscopy are examples of analytical methods guided by light microscopy which analyses the surface chemistry of the fibres. Recent HSE funded work with Raman spectroscopy suggest that some differences in the OH-OH stretching bond in the chemical signature could be helpful discriminating between asbestos and non-asbestos fibres but current experiences with this method show that tremolite is the fibre that gives the least differences. Auger electron microscopy is another surface technique but it must be recognised that the surface chemistry will be influenced by the recent history of the fibre due to weathering and sample preparation. Other analytical methods such as laser-microprobe mass analysis and proton induced X ray emission spectrography offer more penetration and detailed analysis of the fibre chemistry (Spurny, 1986). However , all of the above are specialist techniques which are not widely available and the analysis time per fibre is usually quite long.

4.2 Methods for characterising fibre populations

The absence of any single definitive property or observation for a fibre-by-fibre classification requires that some of the above properties are used for giving a general characterisation of the asbestos and non-asbestos fibre content of a population. The main methods used for this are:

4.2.1 *Macroscopic assessment of asbestos fibres*

The macroscopic appearance of the fibres in the rock is an extremely important observation to make and this assessment can be as valuable as any microscopic assessments as to whether the fibres are asbestos or not. However, it must be remembered that the fibre deposits in the same rocks may vary considerably depending on the local geology. The macroscopic appearance of some tremolite containing rocks is given in Plates 6 -10.

4.2.2 *Optical definition of morphology*

Some effort has gone into developing descriptions of bulk asbestos fibres and these have been used in MDHS 77. It can be seen a variety of morphologies are described and although indicative they are not unique. For example the morphological description/definition as reproduced in section 2.8 could also be applied to non-asbestos para-aramid, while a sample of ground anthophyllite might be deemed to be non-asbestos. Interestingly a range of morphological types seem to be allowed in the definition (needle -like fibres) as well as fibres with splayed ends, representing a range of fibrous habits. For ease of reference interference micrographs of three tremolite materials showing various habits are given in plates 11-13.

4.2.3 *Discriminant analysis based on fibre size and aspect ratio distributions*

Size and aspect ratio distributions of asbestos fibres has been widely investigated as a method of distinguishing between asbestos and non-asbestos fibre populations. These methods were reviewed in an earlier report by Chisholm (1995). It is not surprising that the elongated cleavage fragments (stubby prisms) have a different aspect ratio to asbestos fibres and by measuring fibre length and width and calculating the aspect ratio, differences between these two end populations can be clearly seen. Seigrist and Wylie (1982) applied disriminant analysis methods to determine whether a fibre is asbestos or not, based on its size. The method involves plotting lengths and widths of a random sample of fibres on a log v log scale. The least squares regression line is computed and is of the form:
Log width = F log length -b where F is the slope or index of fibrosity.

The log width parameter was found to be able to separate known asbestos sample and known non-asbestos sample populations with greater than 90% success. To improve the discriminant analysis for non-asbestos particles, the approach was further extended to include the log aspect ratio. Wylie and Schweitzer (1980) applied the method to wollastonite fibres and included an Indian tremolite.

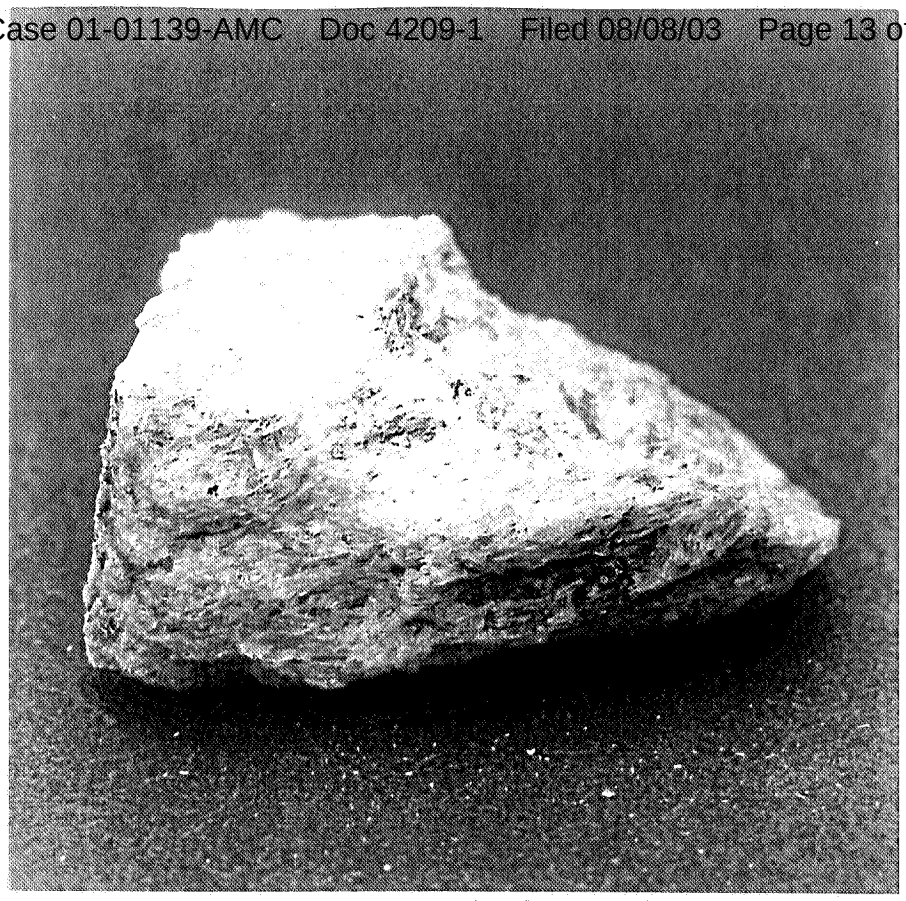


Plate 6: Macroscopic sample of tremolite from :- Shinness

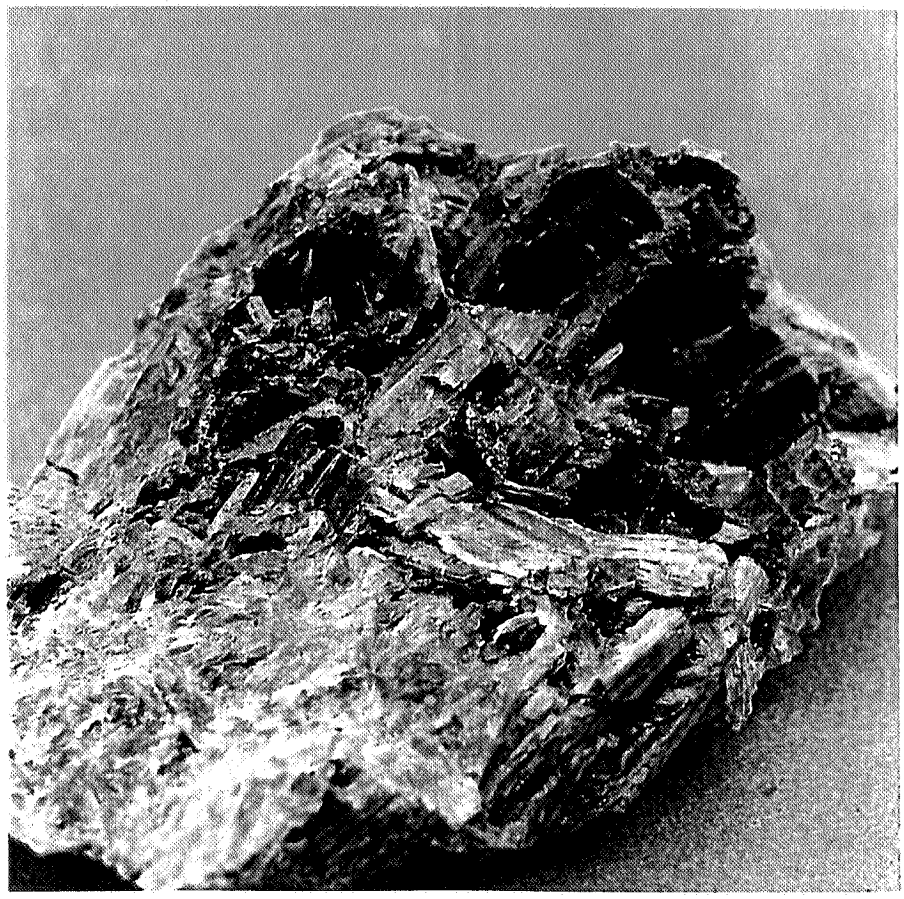


Plate 7: Macroscopic sample of tremolite from :- Dornie, Carr Brae, Inverness